

## Black carbon in estuarine and coastal ocean dissolved organic matter

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### Abstract

We measured black carbon (BC) in ultrafiltered, high-molecular weight dissolved organic matter (UDOM) in surface waters of Delaware Bay, Chesapeake Bay, and the adjacent Atlantic Ocean (U.S.A.) to investigate the importance of riverine and estuarine dissolved organic matter (DOM) as a source of BC to the ocean. BC was 5–72% of UDOM-C ( $27 \pm 17\%$ ), which corresponds to  $8.9 \pm 6.5\%$  of dissolved organic carbon (DOC), with higher values in the heavily urbanized midbay region of the Delaware Estuary and lower yields in the river and coastal ocean. The spatial and seasonal distributions of BC along the salinity gradient of Delaware Bay suggest that the elevated levels of BC in surface water UDOM originate from localized sources, possibly from atmospheric deposition or release from resuspended sediments. BC in UDOM made up 4–7% of the DOC in the coastal Atlantic Ocean, revealing that river–estuary systems are important exporters of colloidal BC to the ocean. The annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean was estimated at  $2.4 \times 10^{10}$  g BC yr<sup>-1</sup>, supporting the hypothesis that the DOC pool is an important contributor of BC to the ocean.

Dissolved organic matter (DOM) in the ocean constitutes one of the largest pools of organic carbon in the biosphere, yet much of its composition remains uncharacterized. In coastal waters, inputs of marine, terrestrial, and anthropogenic organic matter contribute to the complexity of DOM composition. Observations of black carbon (BC) particles in the atmosphere, ice, rivers, soils, and marine sediments suggest that this material is ubiquitous in the environment (Goldberg 1985; Schmidt and Noack 2000; Masiello and Druffel 2001; Mitra et al. 2002). The contribution of BC to the ocean's DOM pool, however, is not known.

BC represents a refractory and chemically complex product of incomplete combustion of fossil fuels and biomass, including vegetation burns and forest fires. BC is defined as a “continuum of partly charred plant material through char and charcoal to graphite and soot particles recondensed from the gas phase” (Seiler and Crutzen 1980, p. 207). Multiple mechanisms introduce BC to the ocean, including atmospheric deposition of land-derived BC aerosols, material transported by river–estuary systems, and marine diesel engine exhaust. Although most BC is deposited near the site of production, long-range transport of BC through rivers and the atmosphere is also possible (Goldberg 1985). BC accumulates in sediments, making up 10–50% of sedimentary organic carbon (Gustafsson et al. 1997; Middelburg et al. 1999) and is much older (2,400–13,900 yr older) than non-

BC material in deep ocean settings (Masiello and Druffel 1998). The radiocarbon age differences between sedimentary BC and other sedimentary organic matter present an unresolved issue on whether the BC that ultimately resides in marine sediments ages primarily within the oceanic dissolved organic carbon (DOC) pool or in soils (Masiello and Druffel 1998).

In an effort to understand the importance of riverine and estuarine DOM as a source of BC to the ocean, the BC component of ultrafiltered, high-molecular weight DOM (UDOM) was measured in surface waters of the Delaware Estuary and Chesapeake Bay (mid-Atlantic, U.S.A.). We present evidence that BC comprises a significant fraction of marine DOM, accounting for a substantial fraction of DOC that has previously remained elusive to chemical characterization.

### Methods

**Study sites**—The Delaware Estuary is a highly urbanized coastal plain estuary, extending 215 km from the mouth of the bay to Trenton, New Jersey, the upstream limit of tidal influence (Fig. 1). Freshwater entering the estuary, with a mean annual discharge of  $550 \text{ m}^3 \text{ s}^{-1}$ , originates largely from the Delaware ( $\sim 58\%$ ;  $320 \text{ m}^3 \text{ s}^{-1}$ ) and Schuylkill ( $\sim 14\%$ ;  $78 \text{ m}^3 \text{ s}^{-1}$ ) rivers, with minor contributions from other individual sources (Lebo and Sharp 1993). Chesapeake Bay, also a coastal plain estuary, discharges more freshwater (mean annual discharge of  $2,280 \text{ m}^3 \text{ s}^{-1}$ ; Schubel and Pritchard 1986) than any other river–estuary system along the U.S. Atlantic coast. The Susquehanna River, which flows into the head of Chesapeake Bay, contributes about half of the total freshwater discharge within the estuary.

**Sampling and analyses**—Size-fractionated DOM was collected at five to seven sites (1 m depth) along the salinity gradient from the Delaware River to the coastal Atlantic Ocean in June 1996, September 1996, March 1997, and May–June 1997 (Fig. 1; Table 1; Mannino and Harvey 2000;

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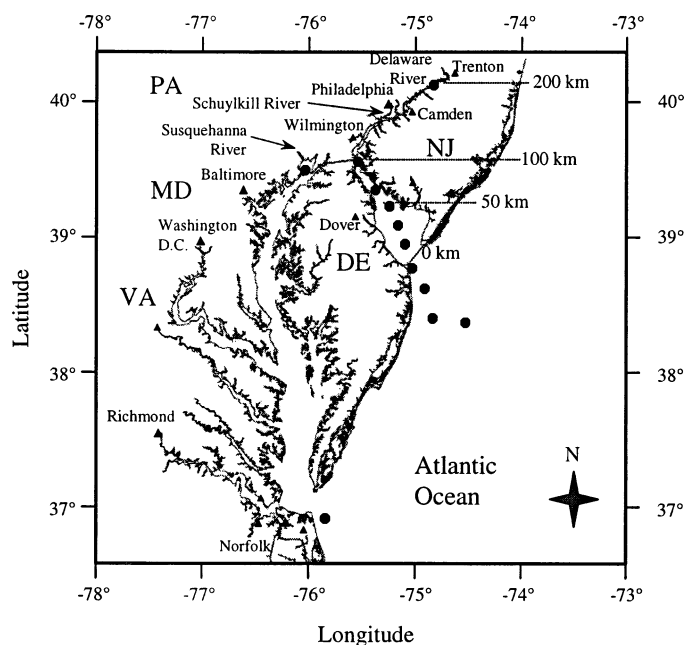


Fig. 1. Map of the Delaware Estuary and Chesapeake Bay, including station locations and designation of urban areas (triangles).

Harvey and Mannino 2001). Single samples were collected from the headwaters of Chesapeake Bay and beyond the Chesapeake Bay mouth in May–June 1997 (Table 1). DOM from filtered water ( $<0.2 \mu\text{m}$ ) was separated into three nominal size fractions— $<1$  kilodalton (kDa), 1–30 kDa, and 30 kDa to  $0.2 \mu\text{m}$ —by tangential-flow ultrafiltration with the use of an Amicon DC-10L unit with S10Y30 (30 kDa; regenerated cellulose membrane) and S10N1 (1 kDa; polysulfone membrane) filters following the methods of Benner et al. (1997) as previously described (Mannino and Harvey 1999; Harvey and Mannino 2001). The two high-molecular weight fractions were concentrated and desalted during ultrafiltration. High-molecular weight DOM samples were stored frozen and lyophilized to dry powders. The ultrafiltration concentration factors (CF; initial volume/concentrate volume) ranged from 37–81 for the 1–30-kDa fraction (CF = 15 for the turbidity maximum station for the June 1996 sampling) and 80–194 for the 30-kDa to  $0.2\text{-}\mu\text{m}$  fraction. The retention coefficient of a 4.4-kDa fluorescently labeled dextran was  $>99\%$  for the S10N1 filter (Mannino and Harvey 2000). The three DOC size fractions accounted for 83–111% of total DOC, which compares well with previous results using similar instrumentation and procedures (Guo and Santschi 1996; Benner et al. 1997). BC was measured only in the 1–30-kDa fraction (UDOM), which constitutes, on average,  $35 \pm 15\%$  of DOC (Harvey and Mannino 2001). The 30-kDa to  $0.2\text{-}\mu\text{m}$  fraction typically accounted for only 1–3% of DOC.

Standards and lyophilized UDOM samples were weighed into silver capsules in triplicate or duplicate and thermally oxidized within a muffle furnace at  $375^\circ\text{C}$  in the presence of air for 24 h to remove non-BC organic matter (Gustafsson et al. 1997). Thermally oxidized and nonthermally oxidized samples were acidified with  $12 \text{ mol L}^{-1}$  HCl vapors for 48 h, oven dried ( $45\text{--}55^\circ\text{C}$ ), and analyzed for carbon content with a CHN elemental analyzer. Thermal oxidation of samples followed by acidification yields BC content, whereas nonthermally treated samples yield total organic carbon (TOC).

### Future considerations

Much work remains to elucidate the source inputs and fates of BC in the ocean. Measures of BC fluxes from the atmosphere and land to rivers, estuaries, and ocean for both particulate and colloidal BC are essential to better constrain the inputs of BC to the ocean. Understanding the role of BC in the ocean's carbon cycle requires that we examine the mechanisms and rates of BC removal, as well as the transfer of BC from dissolved to sedimentary pools. Radiocarbon and other techniques should be used to distinguish the sources of BC within ocean DOM and suspended particles. Detailed structural and isotopic characterization of BC from multiple environments will be required to fully understand the sources and fates of BC in the ocean.